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MEASUREMENT OF RADIATIVE LIFETIMES OF VIBRATIONAL STATES OF SIMPLE IONS

Prof. Rose Marx

Dr. Gérard Mauclaire

Laboratoire de Physico-Chimie des Rayonnements

(associated to CNRS)

Université Paris-Sud

91405 Orsay, France

*Paris - 11 Univ. Orsay
(France)*

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Abstract:

A unique differentially pumped triple cell FT/ICR machine, where production of the ions, storage in a high vacuum trap for variable relaxation times and chemical monitoring of the internal energy content of the ions are separated as well in space as in time, has been shown to be well suited for experimental determination of radiative lifetime of ions.

The monitor ion technique relies on the availability of energetically appropriate ion molecule processes, usually charge or proton transfer reactions. When several levels are populated, only overall lifetimes can be experimentally determined and correction of the raw data for radiative cascade is needed to get individual lifetimes. The reliability of this technique has been demonstrated for $\text{NO}^+(\text{X}, v=1-4)$ where accurate *ab-initio* calculations exist.

For $\text{HCl}^+/\text{DCl}^+(\text{X}, v=1)$ the agreement with theoretical calculation is reasonable. For polyatomic ions our method can only indicate the presence and measure the relaxation rate of the amount of energy needed to drive the monitor reaction. However this proved quite valuable in the case of the acetone ion, revealing the unexpected possibility to store a substantial amount of internal energy for milliseconds. For some triatomic and tetratomic ions like HCO^+ , H_2O^+ , NH_3^+ , our preliminary results have to be confirmed and completed with the newly improved experimental set-up. Reduction of collisional quenching in the relaxation cell by a double differential pumping will allow measurements of lifetimes up to ~one second. Improvement of the detection sensitivity and reduction of mass discrimination in a large mass range, due to the upgrading of the detection console and to a better control of the ions motion, will increase the accuracy and hopefully allow analysis of multi-exponential decays.

Co-Principal Investigators:

Prof. Rose Marx
Dr. Gérard Mauclaire
Laboratoire de Physico-Chimie des Rayonnements
(associated to CNRS)
Université de Paris-sud, 91405 Orsay, France.

Senior Research Participants:

Dr. Serge Fenistein
Dr. Michel Heninger

Junior Research Participants:

Ying Min Yang
Sylvie Jullien

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Main Presentations:

"Reaction and radiative relaxation of ions in their ground electronic state: HCO^+
11th IMSC, Bordeaux, France, September 1988

"Reaction and radiative relaxation of vibrationally excited ions in their ground electronic state"

Japanese Seminar on Photochemistry, Tsukuba, Japan, October 1988

"Experimental determination of lifetimes of vibrationally excited ions"

Colloque Franco-Soviétique: Elementary processes and mechanism of chemical reactions in gas and condensed phase"

November 1990, Tashkent, USSR.

"Tricyclotron: A triple cell FTICR spectrometer.

Ion Trapping in Mass Spectrometry, Sanibel Island, Florida, January 1990

"Radiative lifetimes of vibrationally excited ions using a triple cell FTICR spectrometer"

Conference on Ion Chemistry and Mass Spectrometry

Lake Arrowhead, California, February 1990

"Relaxation and reactions of vibrationally excited and metastable NO^+ ions"

The 38th ASMS Conference on Mass Spectrometry and Allied Topics

June 3-8, 1990, Tucson, Arizona.

"Radiative lifetimes of vibrationally excited and metastable ions"

NATO ASI-Fundamentals of Gas Phase Ion Chemistry, June 25-July 6, 1990,

Mont Sainte Odile, France

"Chemical probing of the internal energy of ions using a triple cell FT/ICR spectrometer"

12th IMSC, Amsterdam, The Netherlands, August 1991

Thesis:

"Etude par Spectrometrie de Résonance Cyclotronique Ionique de réactions et relaxations d'ions à énergie de collision thermique." Michel Heninger, 28/11/1988, Orsay.

Publications:

- 1 "Radiative lifetime for $v=1$ and $v=2$ ground state NO^+ ions
M. Heninger, S. Fenistein, M. Durup-Ferguson, E.E. Ferguson, R. Marx
and G. Mauclaire
Chem. Phys. Letters **131** (1986) , 439
- 2 "Radiative lifetimes of vibrationally excited ions: HCl^+ and $\text{DCI}^+(^2\Pi_{1/2,3/2}^{v=1})$ "
M. Heninger, S. Fenistein, G. Mauclaire, R. Marx and Y.M. Yang
J. Chem. Soc., Faraday Trans. 2, **85**(10) (1989), 1705
- 3 "Radiative relaxation of $\text{NO}^+(X, v=1-4)$ "
S. Fenistein, M. Heninger, R. Marx, G. Mauclaire and Y.M. Yang
Chem. Phys. Letters, **172** (1990) , 89
- 4 "On the Lifetime of Electronically Excited Acetone Molecular Ions"
S. Fenistein, J. Futrell, M. Heninger, R. Marx, G. Mauclaire and Y.M. Yang
Chem. Phys. Letters, **179** (1991), 125
- 5 "Radiative Lifetimes and Reactivity of Metastable $\text{NO}^+(a^3\Sigma^+, v)$ and $\text{O}_2^+(a^4\Pi_u, v)$ "
R. Marx, Y.M. Yang, G. Mauclaire, M. Heninger and S. Fenistein
J. Chem. Phys., **95** (1991), 2259

The objective of this research was to experimentally determine radiative lifetimes of vibrational states of ions. The possibility of such measurements had been demonstrated for the first time using the monitor ion technique in a three stages ICR spectrometer (1). It was proposed to modify and upgrade the experimental device for a better accuracy and a larger range of lifetimes, and to apply the method to simple ions like NO^+ , H_2O^+ , CO_2^+ , NH_3^+ ,...

INSTRUMENTATION:

The more recent state of the set-up is the following:

- The ions to be studied are produced in a first ICR cell by a pulsed electron beam. To allow for multiphoton ionisation, a high pressure but short residence time ion source has been added.

- Mass selected ions are drifted into a UHV pumped relaxation/detection cell (3×10^{-9} Torr) with FT-ICR detection capability. Double differential pumping insures a pressure gradient of ~ 5000 with the ion source. Ions can be stored there virtually collision free for variable relaxation times, up to $\sim 1\text{s}$.

- After this relaxation period, the ions are drifted into the third cell where they undergo reaction with a suitable monitor gas. The monitor ion technique is based on the reasonable assumption that at thermal energies, reactions like charge or proton transfers are much faster for exothermic than for endothermic processes. The product ion, monitored as a function of the relaxation time, then reflects the decay of the primary ions having internal energy higher than the endothermicity of the reaction. Here also, a double differential pumping prevents the monitor gas to significantly leak into the relaxation cell (pressure gradient = ~ 3500).

- The packet of reactant and product ions is then drifted back into the high vacuum central cell, where mass analysis and quantification are performed using the FT-ICR detection.

As long as all other parameters are kept constant during an experiment (ion production, ion monitoring, and ion detection) the variation of the relative intensity of the monitor ion signal reflects only the processes occurring during the relaxation period. In particular, even if only a fraction of the excited state is converted into monitor ions in the reaction cell (slow reaction, or competing reactions, or partial collisional deactivation) the method is still valid as long as the conversion stays constant, which is the case since the monitor gas pressure and the reaction time are kept constant.

It has to be outlined that the instrumentation part of this program could not be completed beforehand, but rather had to take place gradually all along the four years of this program, guided by the expertise gained at each stage of these new type experiments. This evolution appears clearly in the annual interim reports:

- $\text{HCl}^+/\text{DCI}^+$ (2) and HCO^+ were studied with the capacitive bridge detector used in our initial study of NO^+ , since the FT/ICR console, purchased with AFOSR money, was delivered in January 1989 and was operational only 18 months after the starting date of the contract. This delay was due to the necessary adaptations of the commercial set-up to our special needs and to the design and construction of a new type cubic detection cell allowing drift input from and drift output to both adjacent cells.

- For all the ions studied so far we have used the initial vacuum system, with only single differential pumping of the central cell. As the pressure gradient between the relaxation cell and each adjacent cell was only 150, collisional relaxation and reactions with the background gas were no more negligible compared to radiative relaxation for long lived ions, so that tedious and in some cases hasardous corrections had to be done.

- During the last year double differential pumping of the central cell has been introduced as well as multiphoton ionisation capability. Ion detection has been improved, with an upgrade of the detection console by its constructor, and a better control of the ions in the central cell. All ions, including light ones (CH_4^+ , H_2O^+ , NH_3^+ ,) can now be detected in a single scan in broadband mode at 1.5 Tesla, with practically no mass discrimination.

LIFETIMES MEASUREMENTS:

Radiative lifetimes and reactivity of *vibrationally excited ions* in their ground electronic state as well as *electronically excited metastable ions* have been studied.

A) Diatomics

Lifetimes and reactivity of $\text{NO}^+(\text{X}, v=1-4)$

Measurement of the radiative lifetimes of the two first levels of this ion (1) with the initial version of the Tricyclotron had been the starting point of these studies. With the better sensitivity of the new detection cell and FT console, two more levels could be measured (3). In addition, a method for correction of the raw experimental data for radiative cascade from the upper vibrational levels and for quenching (and/or reaction) by the small amount of gas leaking from the ion source and reaction cell into the relaxation cell has been worked out, and proved to be reliable. The lifetimes obtained for $v = 1$ to 4, respectively 83, 42, 26 and 22 ms, are in good agreement with the *ab initio* calculations: 88, 45, 31, and 24 milliseconds (Rosmus and coll., Langoff and coll), and with the more recent values of: 90, 49, 30, 25 ms, obtained by Bowers and coll.

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Lifetime and reactivity of $\text{NO}^+(\text{a}^3\Sigma^+)$ and $\text{O}_2^+(\text{a}^4\Pi_u)$

Radiative lifetimes of (100 ± 20) ms and (135 ± 25) ms have been found for $\text{NO}^+(\text{a}^3\Sigma^+)$ $v \geq 1$ and $v \geq 0$ respectively, with Ar and CO_2 as monitor gases. The overall reaction rate of $\text{NO}^+(\text{a}^3\Sigma^+)$ $v \geq 1$ with Ar ($6.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) is one order of magnitude larger than the rate of $v=0$ determined in flowing afterglows. CO_2 reacts at collision rate. For O_2^+ the overall lifetime of $v \geq 0$, determined with Ar as monitor, is (30 ± 6) ms in between the two values (7 and 130 ms) found by Bustamente *et al.*, using the photodissociation technique. Until the recent calculations of Yarkony *et al.*, (JCP Nov. 1991) the experimental results on NO^+ could only be compared to values calculated using a very crude perturbation model (5). Surprisingly the new, much more elaborate calculations give quite similar values (400 ms for $v=0$). The reasons for our shorter lifetimes are not clear at the moment.

B) Small polyatomics

HCO^+ : For this astrochemically important ion a whole set of monitor molecules whose proton affinities match quite nicely the HCO^+ vibrational energy scale has been used. Observed radiative lifetimes of (35 ± 5) ms, (12 ± 2) ms, and (4 ± 1) ms have been tentatively attributed to the $v = 1, 2$, and 3 of the CO stretching mode. It has been shown with a computer program written to analyze multiexponential decays, that much better signal to noise ratios are needed to decide if the observed decays are multiexponentials, i.e., if mixed modes are involved. In addition, a very long lived mode (> 500 ms) has been observed, but could not be quantitatively determined due to insufficient differential pumping at that time. However, the fact that part of the energy stays in the ions for a very long time indicates that at least up to ~ 1 eV there is no energy transfer from the long lived mode to the short lived ones, in the absence of collisions.

CO_2^+ : The lifetime of CO_2^+ has been measured using Kr as monitor gas. Since the monitor ion signal was found to stay constant over 100 ms relaxation time, the lifetime must be larger than ~ 800 ms. To measure such long lifetimes the pressure in the relaxation cell was at that time too high, at least by one order of magnitude. In the meantime P. Rosmus and G. Chambaud calculated the potential energy surfaces for CO_2^+ . Experimentally however, the fraction of monitor ions formed by ions excited in the symmetric modes (infinite lifetimes) could be too important and therefore obscure the decays corresponding to the asymmetric modes.

H_2O^+ : For most of the possible monitor gases there is a competition between charge transfer (CT) and proton transfer (PT). For N_2O although the endothermicity is almost the same for PT and CT (0.27 and 0.25 eV respectively), the PT channel is about three times more efficient.

The overall lifetime determined with PT as monitor reaction is ~ 24 ms.

NH₃⁺: For NH₃⁺ preliminary experiments have been performed with the old version of the trieyclotron and the results are in reasonably good agreement with the calculations published a few months later by P. Botschwina. More elaborate experiments are needed and to avoid the problems due to the population of several vibrational modes, the multiphoton ionization capability recently added to our machine should be used to produce the ions selectively.

C) A large polyatomic: (CH₃)₂CO⁺⁺

In connexion with a crossed beam study at Delaware (Pr. J. Futrell), we have determined radiative lifetimes of electronically excited acetone ions produced by 30 eV electrons, using two monitor reactions: Collision induced dissociation (CID) with He, and charge transfer reaction with O₂.


CID monitors (CH₃)₂CO⁺⁺ ions with at least 2.9eV of internal energy while reaction with O₂ needs only 2.4eV to occur. The corresponding lifetimes are respectively 4 and 14ms. The threshold energy for CID is ~0.15eV, indicating a barrier to dissociation (4).


CONCLUSIONS and PROSPECTS:

A unique differentially pumped triple cell FT/ICR machine, where production of the ions, storage in a high vacuum trap for variable relaxation times, and chemical monitoring of the internal energy content of the ions are separated as well in space as in time, has been shown to be well suited for experimental determination of radiative lifetime of ions. During this contract, problems limiting the accuracy and applicability of the method have been assessed and largely solved with extensive modifications of the experimental device.

The method, relies on the availability of energetically appropriate ion molecule processes, usually charge or proton transfer reactions. Proved to be reliable for NO⁺ ions, it has been applied to other diatomics, triatomics and one large polyatomic ion. The results have been compared with theoretical calculations when available. Our technique is easier to apply and works better when only one internal mode is involved, i. e., for diatomics which also happens to be well described by *ab-initio* calculations. When such calculations are becoming costly and difficult, starting with triatomics, the existence of several internal modes usually makes the monitor ion results difficult to analyze. For large polyatomic ions, *ab-initio* calculations are out of question, and our method can only test the availability and relaxation of the amount of energy needed to drive the monitor reaction. However this proved quite valuable in the case of the acetone ion, revealing the unexpected possibility to store a substantial amount of internal energy for milliseconds.

Because of limited performances of the experimental device at the time of their obtention, some of our results are only preliminary. It should now be possible to confirm, complete and publish most of them, particularly HCO⁺/DCO⁺, H₂O⁺, NH₃⁺, and also to investigate new systems.


Professor R. Marx


Doctor G. Mauclaire